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**Transmission Message:**

**Our Docket No.:** 113PUS05900P  
**In Re Application:** K. R. Lassila, et al.  
**Serial No.:** 09/975,135  
**Filed:** 11 October 2001  
**Group Art Unit:** 1714  
**Examiner:**  
**For:** Acetylenic Diol Ethylene Oxide/Propylene Oxide Adducts  
and Processes for Their Manufacture

**Included Documents:**

Information Disclosure Statement by Applicant  
Japan Patent 11-352703  
Japan Patent 09150577 (abstract)  
Japan Patent 03063187  
US Patent 4,241,224  
US Patent 4,668,423  
US Patent 4,814,514  
Japan Patent 02636954  
US Patent 4,374,920  
US Patent 4,833,067  
US Patent 5,756,267  
US Patent 5,650,543  
Japan Patent 2621662  
Leeds Article

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Sheet 1 of 1

FORM PTO-1449 (Modified)	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTY. DOCKET NO. >113PUS05900P	SERIAL NO. >09/975,135
<b>INFORMATION DISCLOSURE STATEMENT BY APPLICANT</b> (Use several sheets if necessary)		APPLICANT >K. R. Lassila, et al.	
		FILING DATE >11 October 2001	GROUP >1714

(37 CFR 1.98(b))

## U.S. PATENT DOCUMENTS

EXAM- INER INITIAL	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
	4 2 4 1 2 2 4	12/23/80	Newkirk, et al.			
	4 6 6 8 4 2 3	5/26/87	Drozdz et al.			
	4 8 1 4 5 1 4	3/21/89	Yokota, et al.			
	4 3 7 4 9 2 0	2/22/83	Wanai, et al.			
	4 8 3 3 0 6 7	5/23/89	Tanaka, et al.			
	5 7 5 6 2 6 7	5/26/98	Matsuda, et al.			
	5 6 5 0 5 4 3	7/22/97	Medina			

## FOREIGN PATENT DOCUMENTS

	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION
						YES NO
	JP 11 3 5 2 7 0 3	12/24/99	Japan			X
	JP 9 1 5 0 5 7 7		Japan (abstract)			
	JP 3 0 6 3 1 8 7	12/19/97	Japan			X
	JP 2 6 3 6 9 5 4	4/25/97	Japan			X
	JP 2 6 2 1 6 6 2	4/4/97	Japan			X

## OTHER DOCUMENTS (Including Author, Title, Date, Pertinent Pages, Etc.)

	M. W. Leeds, et al., "Acetylenic Nonionic Surfactants," Dec. 1965, pp 236-242

EXAMINER

DATE CONSIDERED

EXAMINER: Initial citation considered. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

PATENT: 113PUS05900P

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLI-  
CATION OF : K. R. LASSILA, ET AL.

SERIAL NO. : 09/975,135 : GRP. ART UNIT: 1714

FILED : 11 OCT 2001 : EXAMINER:

FOR : ACETYLENIC DIOL ETHYLENE OXIDE/PROPYLENE OXIDE  
ADDUCTS AND PROCESSES FOR THEIR MANUFACTURE

Assistant Commissioner for Patents  
Washington, D.C. 20231

CERTIFICATE OF FACSIMILE TRANSMISSION	
I CERTIFY THAT THIS PAPER IS BEING FACSIMILE TRANSMITTED TO THE PATENT AND TRADEMARK OFFICE ON THE DATE SHOWN BELOW:	
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Signature of person sending paper	

Sir:

INFORMATION DISCLOSURE STATEMENT  
AND PRELIMINARY STATEMENT

The present application is a continuation-in-part of Application Serial No. 09/304,607 filed 4 May 1999 which issued 6 Nov 2001 as US 6,313,182 B1. Presently pending Claims 1-22 correspond to many of those that were originally presented in Application Serial No. 09/304,612 filed 4 May 1999. (The specifications of Appln. '607 and Appln. '612 are essentially identical.) Claims 1-10 are directed to a method for making an acetylenic diol ethylene oxide/propylene oxide (EO/PO) adduct that is capped with PO units by reacting an acetylenic diol EO adduct with PO in the presence of a trialkylamine catalyst. Claims 11-22 are directed to acetylenic diol ethylene oxide/propylene oxide (EO/PO) adducts which contain isobutyl or isoamyl groups and Claims 13-22 are directed to such adducts capped with the PO units.

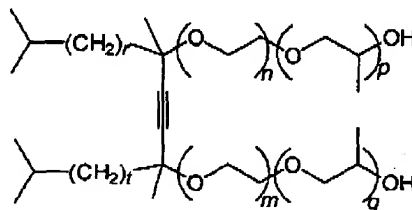
In an Appln. '612 Office Action mailed 14 March 2001, Examiner R. Keys of Art Unit 1621 rejected pending Claims 1-59 under 103(a) as being unpatentable over Tanabe (JP 11-352703) in view of JP 09150577 (abstract); Matsumoto (JP 03063187); Newkirk (US 4,241,224); and Drozd (US 4,668,423) and further in view of Yakota (US 4,814,514); the

Leeds publication; and Kinoshita (JP 02636954), copies enclosed. Appln. '612 went abandoned by failure to respond to the Office Action.

The acetylenic diol ethylene oxide/propylene oxide adducts made according to independent method Claim 1 have an acetylenic diol moiety derived from 2,4,7,9-tetramethyl-5-decyne-4,7-diol or 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol.

In support of method Claims 1-10, the Examiner is directed to Applicants' Example 1 which shows that reacting an acetylenic diol/EO adduct with 7 moles of PO using a trialkylamine catalyst essentially yielded only a product capped with only two PO units. See in particular the discussion at pages 21/16 - 22/2 of the present Application. See also 13/11-13.

The acetylenic diol ethylene oxide/propylene oxide adducts of independent Claim 11 have the structure



where  $r$  and  $t$  are 1 or 2,  $(n + m)$  is 1.3 to 30 and  $(p + q)$  is 1 to 10, the ethylene oxide and propylene oxide units being distributed along the alkylene oxide chain in blocks or randomly. The acetylenic diol ethylene oxide/propylene oxide adducts of independent Claim 12 have the ethylene oxide and propylene oxide units distributed along the alkylene oxide chain in blocks.

In support of Claims 11-22, the Examiner is directed to the adduct of Example 22 in the present application which corresponds to that taught by Matsumoto's Example 4 although Matsumoto does not teach a method for its preparation or whether the adduct is a block or random copolymer. Applicants believe Matsumoto (JP 03063187) is the only reference of record showing an actual working example of an EO/PO adduct of an acetylenic diol. The acetylenic diol used in Matsumoto and Applicants' Example 22, namely 3,6-dimethyl-4-hexyne-3,6-diol, contains an ethyl group. Applicants' Claims 11 and 12 require an isobutyl or isoamyl group. The adduct of Example 22 was prepared using  $\text{BF}_3$  catalysis producing the PO capped EO/PO adduct. NMR analysis determined there were 9.6 EO moles and 1.9 PO moles in the reaction product. Thus the adduct of Example 22 corresponds to Matsumoto's adduct which is stated to contain 8 to 12 EO units and 1 to 2 PO units.

It can be seen from Comparative Example 25 and Example 26 of the present Application that the 1 wt% solution of the Example 5 PO capped EO/PO adduct (compared to that of the 5 wt% solution of the Matsumoto Example 22 PO capped EO/PO adduct) showed superior performance at all surface creation rates at one-fifth the use level. It would not be anticipated based on the prior art that modification of the hydrophobic group, i.e., the acetylenic diol moiety, by replacing ethyl groups with isobutyl groups would have such an advantageous effect in reducing dynamic surface tension.

As stated, Claims 1-59 of Appln. '612 were rejected under 103(a) as being unpatentable over Tanabe (JP 11-352703) in view of JP 09150577 (abstract); Matsumoto (JP 03063187); Newkirk (US 4,241,224); and Drozd (US 4,668,423) and further in view of Yakota (US 4,814,514); the Leeds publication; and Kinoshita (JP 02636954). Applicants submit that the references as combined and relied upon by Examiner Keys do not teach or suggest the claimed subject matter as a whole. Applicants again submit that the necessity of constructing such a strained, complex combination of eight references to support a 103 rejection is based on hindsight disclosure of Applicants' invention and is indicative of nonobviousness.

With regard to Claims 1-10, the combination of references does not teach or suggest the claimed subject matter, namely, that using a trialkylamine catalyst in the propoxylation of an acetylenic diol/EO adduct surprisingly yields essentially only a product which is capped with two PO units as shown Applicants' Example 1.

While the Tanabe reference on page 11 suggests adding EO, PO, or a mixture of EO/PO to acetylenic alcohol, it only teaches with more specificity the EO adducts on page 12 and shows a mixture of EO adducts on page 19. More importantly, Tanabe is deficient with respect to any teaching or suggestion on how to make these adducts, especially the EO/PO materials. Examiner Keys attempted to remedy this deficiency of Tanabe by reference to JP '577 and Matsumoto for showing EO/PO surfactants. JP'577 merely shows an acetylenic glycol adduct of Formula I in which R2 can be either the EO derivative or the PO derivative. This reference does not teach or suggest the mixed EO/PO derivative. Nevertheless, Matsumoto in Example 4 on page 26 shows the (EO)<sub>8-12</sub>/(PO)<sub>1-2</sub> adduct of 3,6-dimethyl-4-octyne-3,6-diol. However, and most importantly, neither JP '577 nor Matsumoto teach how to make alkylene oxide adducts of acetylenic glycols in general or specifically EO/PO adducts.

Examiner Keys attempted to remedy this deficiency of JP '577 and Matsumoto regarding the EO/PO mixed adducts by reliance on the Drozd and Newkirk references as

teaching that surfactants having both EO and PO groups can be obtained by reacting alcohols with mixtures of EO and PO. Drozd teaches alkoxyating primary aliphatic alcohols (Col 3/42+) using an EO/PO mixture that is added to obtain a random distribution of these units (4/13-25). Drozd teaches the use of ionic, alkaline catalysts, especially strong bases or salts thereof with weak acids, preferably potassium, sodium and quaternary ammonium salts and hydroxides (4/33-40). In Example 1 Drozd specifically shows the use of 85% potassium hydroxide.

Newkirk is directed to alkoxyating an intermediate material, namely glycerol-1,3-dialkylether, with a mixture of EO and PO to obtain synthetic fiber lubricants and processing aids. Newkirk's Examples 1-3 show the use of aqueous potassium hydroxide as a catalyst for this reaction. The intermediate glycerol-1,3-dialkylether is made using BF<sub>3</sub> catalyst.

Most importantly, neither Drozd nor Newkirk contains any teaching or suggestion for making an acetylenic diol EO/PO adduct using a trialkylamine catalyst.

Examiner Keys attempted to remedy the deficiency of all the prior references with regard to the use of a trialkylamine as a catalyst for making an acetylenic diol EO/PO adduct by recitation of a third layer of references. Yakota at 3/58-63 does not, as the Examiner seemed to allege, teach the use of trialkylamine as a catalyst for adding EO and PO groups to a surfactant. This passage clearly pertains to reacting an alkylene oxide derivative (VII) with a glycidyl ether (VIII) using triethylamine or boron trifluoride-ether complex to make compounds of formula (IX). This is not a teaching or suggestion with regard to the reaction of an EO/PO mixture with alcohol functionality.

The Examiner's attention is directed to 4/1-15 of Yakota which teaches that compounds (I) are produced by the addition of alkylene oxides of 2-4 carbon atoms to compounds (IX). "The reaction may be carried out in the presence of a conventional basic or acidic catalyst." In fact, Yakota's Example shows the use of potassium hydroxide as such conventional catalyst. Thus, Yakota is also deficient with respect to any teaching or suggestion regarding the use of a trialkylamine as a catalyst for reacting alkylene oxide with an acetylenic diol.

The above deficiencies of Yakota and the other primary and secondary references cannot be remedied simply by having one of ordinary skill in the art look to methods known in the art for making acetylenic non-ionic surfactants wherein an acetylenic alcohol is reacted with ethylene oxide or propylene oxide in the presence of a trialkylamine catalyst. The references themselves must provide the direction to look for such methods. Applicants submit that Tanabe, JP '577, Matsumoto, Newkirk, Drozd and Yakota do not provide any

direction or incentive for a worker skilled in the art to seek out this technical information. The Examiner is using the hindsight of Applicants' claimed invention regarding the use of trialkylamine catalysts to provide the necessary direction to Leeds and Kinoshita.

Leeds only pertains to the reaction of EO with acetylenic alcohols. There is no teaching or suggestion with regard to reactions involving PO. On page 239, Leeds teaches that the base-catalyzed cleavage of the acetylenic diols is of importance in the case of a strong-based catalysts such as sodium and potassium hydroxides but is of minor importance when using tertiary amine catalysts at 45 to 70°C. Kinoshita (page 3 of the translation) teaches that amine catalysts are inactive for the addition of PO to acetylenic diols; they are only effective for the addition of EO to these materials. Kinoshita teaches the use of Lewis acids such as BF<sub>3</sub> for the addition of PO to acetylenic diols and not for the addition of PO to acetylenic glycol EO adducts.

In view of the above comments Applicants submit they have presented unexpected results in supporting the patentability of pending Claims 1-10 directed to a method for making acetylenic diol EO/PO adducts that contain 2,4,7,9-tetramethyl-5-decyne-4,7-diol or 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol as the acetylenic moiety and are capped with two PO units. Accordingly, Applicants request allowance of Claims 1-10.

With regard to Claims 11-22 the combination of references does not teach or suggest the claimed subject matter as a whole, namely the defined acetylenic diol EO/PO adducts having improved dynamic surface tension reducing properties, improved defoaming ability and unexpectedly improved surfactant efficiencies. While several of the references suggest acetylenic diols reacted with EO or PO, or both, they only show acetylenic diol EO adducts. Matsumoto is believed the only reference showing an acetylenic diol EO/PO adduct. The fact that the claimed adducts contain 2,4,7,9-tetramethyl-5-decyne-4,7-diol or 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol as the acetylenic moiety patentably distinguishes over Matsumoto as pointed out above.

New examples 54-55 present additional dynamic surface tension ( $\gamma$ ) data, foam data and surfactant efficiency ( $\rho C_{20}$ ) data for various polyethoxylated acetylenic diols and for polyethoxylated/polypropoxylated acetylenic diols of the present Application. The following table incorporates data from the present Application regarding acetylenic diol EO and EO/PO adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol (S-104). The data for the all ethoxylated S-104 adducts, i.e., only EOs, are in *italics*.

Ex	Table Appln	R or B	EO Moles	PO Moles	EO & PO	$\rho C_{20}$	$\gamma$ 0.1 b/s	$\gamma$ 1 b/s	$\gamma$ 6 b/s	$\gamma$ 15 b/s	$\gamma$ 20 b/s	RM Foam (cm) Initial (t to o)
53A	8		5.1	-	5.1	3.95	35.1	36.2	38.1	42.0	44.4	1.6 (0.7cm)
54A	9		5.5		5.5	3.90	36.6	37.7	40.0	42.8	42.3	1.5 (34s)
53B	8	B	5.1	0.4	5.5	3.74	34.8	35.8	37.9	42.0	44.4	1.4 (0.3cm)
			6.0	-	6		-	-	-	-	-	-
53C	8	B	5.1	0.9	6	3.72	34.9	35.9	38.2	42.7	45.3	1.4 (27s)
54B	9		6.5	-	6.5	3.78	38.2	39.4	41.9	45.2	45.2	1.5 (32s)
53D	8	B	5.1	1.4	6.5	3.79	34.6	35.9	38.3	42.0	44.5	1.2 (21s)
54C	9		7.1	-	7.1	3.84	38.8	40.1	42.6	45.7	45.3	1.5 (32s)
53E	8	B	5.1	2.0	7.1	4.13	34.0	35.3	37.6	41.5	43.3	0.6 (6s)
54D			15.0	-	15	3.57	45.9	47.6	49.9	52.4	53.7	1.5 (147s)
39	7	R	5.0	10.0	15.0	4.50	33.4	33.7	39.9	46.1	48.2	0.5 (1s)
40	7	B	5.0	10.0	15.0	4.58	34.3	37.2	40.5	43.1	45.7	0.5 (10s)
54E			17.0	-	17	3.40	46.9	48.6	50.6	52.8	54.1	1.5 (30s)
41	7	R	15.0	2.0	17.0	4.20	32.3	36.0	43.8	49.0	50.7	4.5 (>300s)
42	7	B	15.0	2.0	17.0	5.04	30.4	36.8	42.9	47.5	49.5	5.3 (>300s)
54F			25	-	25	3.34	49.8	51.6	53.3	55.2	56.3	1.3 (59s)
43	7	R	15.0	10.0	25.0	4.42	31.0	33.8	44.5	48.3	52.8	2.8 (>300s)
44	7	B	15.0	10.0	25.0	4.35	30.7	35.5	45.6	52.0	54.9	4.0 (>300s)

The data in the preceding table are based on the acetylenic diol structure in which r and t are both one, i.e., the S-104 molecule. It can be seen from the data that those materials which incorporated PO units in place of some of the EO units, i.e., the overall number of alkylene oxide units being the same, had lower dynamic surface tension values than those in which the material contained just EO units. In addition, the EO/PO adducts of the base S-104 molecule having 6.5 to 15 total EO and PO units demonstrated lower foam levels initially with this foam breaking faster than the corresponding all EO/S-104 examples.

The efficiency ( $\rho C_{20}$ ) data show that EO/PO derivatives having greater than 1 mole of PO exhibited higher efficiencies than their counterparts which contained only EO.

The following table incorporates data from the present Application regarding acetylenic diol EO and EO/PO adducts of 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol (S-124). The data for the all ethoxylated S-124 are in *italics*.



Ex	Table Appln	R or B	EO Moles	PO Moles	EO & PO	$\rho C_{20}$	$\gamma$ 0.1 b/s	$\gamma$ 1 b/s	$\gamma$ 6 b/s	$\gamma$ 15 b/s	$\gamma$ 20 b/s	RM Foam (cm) Initial (t to o)
54G	10		7.0	-	7	4.45	27.3	27.9	30.1	36.3	35.2	4.9 cm (>300s)
45	7	R	5	2	7	4.39	27.2	28.2	33.5	42.5	45.4	2.4 cm (0.2 cm)
46	7	B	5	2	7	4.42	27.4	28.5	32.5	37.7	37.2	3.0 cm (0.3 cm)
54H	10		15.0	-	15	4.28	33.6	38.4	42.3	45.8	42.7	3.0 cm (>300 s)
47	7	R	5	10	15	4.57	30.8	31.8	40.8	52.8	55.1	1.8 cm (>300 s)
48	7	B	5	10	15	4.56	32.1	33.4	40.3	51.6	55.4	1.4 cm (>300 s)
54J	10		17.0	-	17	4.10	36.3	40.6	44.0	47.5	46.3	3.0 cm (>300 s)
49	7	R	15	2	17	4.36	28.0	30.5	40.8	47.5	50.2	2.6 cm (>300 s)
50	7	B	15	2	17	4.17	28.6	31.1	42.5	47.4	50.0	2.5 cm (>300 s)
54K	10		25.0	-	25	3.96	42.5	45.5	48.1	50.9	52.5	2.1 cm (>300 s)
51	7	R	15	10	25	4.58	30.1	32.8	43.2	46.7	45.5	2.0 cm (>300 s)
52	7	B	15	10	25	4.55	29.9	33.7	41.4	46.9	48.8	4.8 cm (>300 s)

The data in the preceding table are based on the acetylenic diol structure in which r and t are both two, i.e., the S-124 molecule. It can be seen from the data that those materials which incorporated PO units in place of some of the EO units, i.e., the overall number of alkylene oxide units being the same, had lower surface tension values than those in which the material contained just EO units. In addition, the EO/PO adducts of the base S-124 molecule having 7 and 15 total EO and PO units demonstrated lower foam levels initially and no increase in foam persistence when compared to the corresponding all EO/S-124 examples. The EO/PO adducts of the base S-124 molecule having 17 and 25 total EO and PO units demonstrated comparable foam levels and no increase in foam persistence when compared to the corresponding all EO/S-124 examples, except for Example 52.

The efficiency ( $\rho C_{20}$ ) data show that for products containing 15 moles of EO/PO and more, those containing PO exhibited higher efficiencies than their counterparts which contained only EO.

The data demonstrates that the acetylenic diol EO/PO adducts of the invention afford improved dynamic surface tension reduction in aqueous solution in the many applications disclosed in the present application. Moreover, the acetylenic diol EO/PO adducts were unexpectedly more efficient than the corresponding all EO adducts. In addition, some of the acetylenic diol EO/PO adducts also manifested lower foaming, an important feature in some of the applications.

The previous remarks regarding the combination of references relied upon by Examiner Keys are incorporated here.

In view of the above data and comments Applicants submit they have presented unexpected results in support of the patentability of pending Claims 11-22 directed to the acetylenic diol EO/PO adducts that contain 2,4,7,9-tetramethyl-5-decyne-4,7-diol or 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol as the acetylenic moiety. Accordingly, Applicants request allowance of these claims.

Also pending is Application Ser. No. 09/477,600 entitled "Acetylenic Diol Ethylene Oxide/Propylene Oxide Adducts And Their Use In Photoresist Developers", in which Claims 14-19 were finally rejected by Examiner H. Le. The rejection was under 103a based on Wanat (US 4,374,920), Tanaka (US 4,833,067) or Matsuda (US 5,756,267). Medina (US 5,650,543), Kohei (JP 2621662) and Leeds ("Acetylenic Nonionic Surfactants") were cited to show related surfactants. Copies of these references are enclosed.

Believing this case is in condition for allowance, Applicants solicit an action to that effect.

Respectfully submitted,



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